



**PAN, natural radioactivity,  
and other data sets:  
Summary of recent field  
activities –**

Jeff Gaffney and N. A. Marley

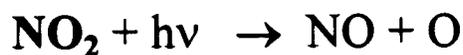
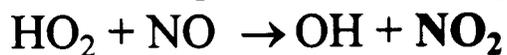
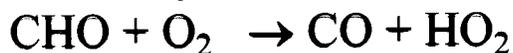
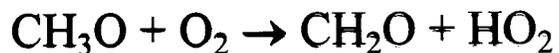
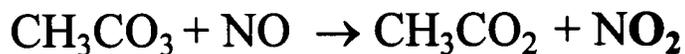
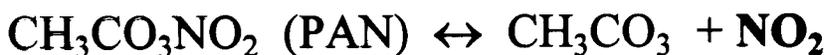
Atmospheric Research Section  
Environmental Research Division  
Argonne National Laboratory  
[gaffney@anl.gov](mailto:gaffney@anl.gov)

## WHY ARE PANs IMPORTANT?

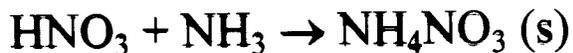
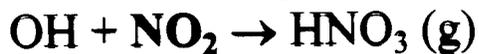
Chemically a trapped peroxy radical.

Coupled to ozone formation.

PAN is a direct measure of photochemical activity.



NOTE:  $\text{OH} + \text{RH} + \text{O}_2 \rightarrow \text{RO}_2 \rightarrow \rightarrow \rightarrow \text{Oxidants}$



## **MAJOR FIELD STUDY - DATA SETS**

### **Mexico City – PAN GC/ECD**

*Atmospheric Environment*, **33**, 5003-5012  
(1999).

### **Phoenix – 1998**

*Atmospheric Environment*, **36**, 825-833  
(2002).

### **Centerton, NJ – 1999**

**AMS - 2002**

### **Central California Oxidant Study -2000**

### **Deer Park, TX – 2000**

**AMS-2002- 7Be and ozone data.**

### **Salt Lake City – 2000**

### **Phoenix – 2001**

## **INSTRUMENTATION**

Fast GC/Luminol system for PANs and NO<sub>2</sub>  
Nitrogen Oxides – NO, NO<sub>y</sub> - ozone chemiluminescence

VOC – Canister samples – Paul Doskey

Ozone – UV absorption

CO – NDIR

UV-B – RB Meter

MFRSR – Yankee Scientific

Nephelometer – (on loan from PNNL!).

Olefin Monitor – Preliminary at Phoenix 2001

Aethalometer – 7 channel aerosol – Black Carbon –  
Anderson

Meteorology – T, RH, WS, WD...SODAR, RASS – Rich  
Coulter

Aerosol Samplers – Sierra Impactors – <sup>7</sup>Be (gamma)  
Beta and Alpha for <sup>210</sup>Bi and <sup>210</sup>Po

**Coming Soon...** TDLAS System – Telescope Optics and  
Herrick Cell.

# **AUTOMATED ANALYSES OF PANs**

**Gas Chromatography - Electron Capture Detection**

**Two-cc Sample Analyzed Every 30 min.**

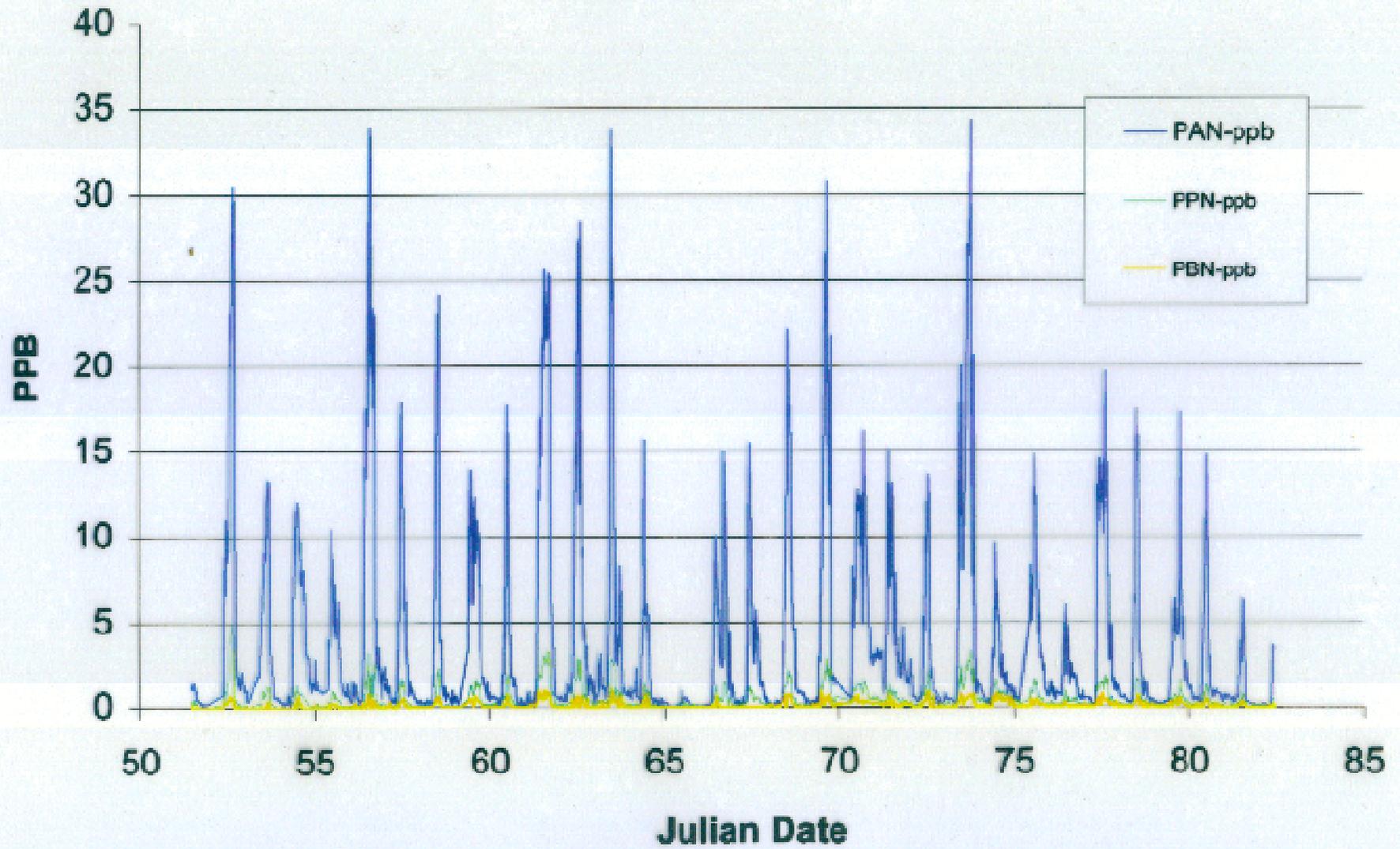
**Automated Sampling Valve**

**Over 1380 analyses**

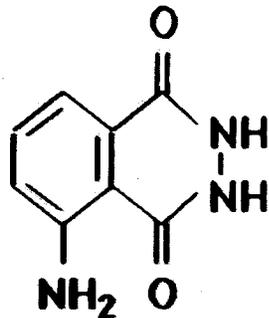
**Sampling Site - Instituto Mexicano de Petroleo  
Northwestern-Central Mexico City**



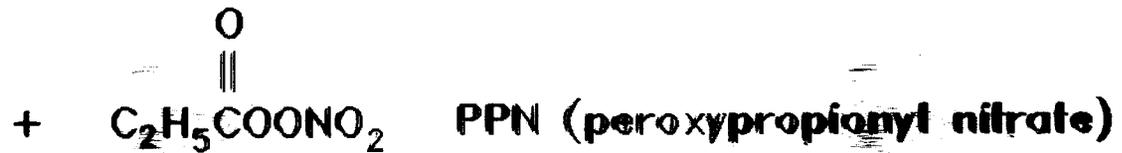
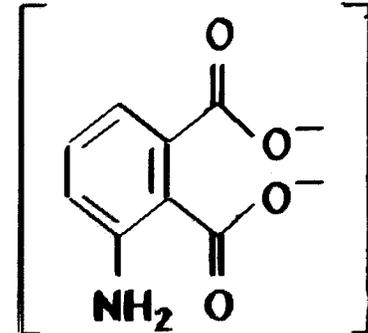
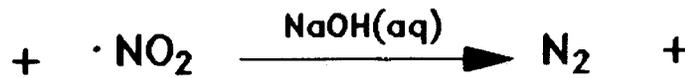
### PANs - Mexico City



# LUMINOL CHEMILUMINESCENCE



**(5-amino-2,3-dihydro-phthalazine-1,4-dione)**

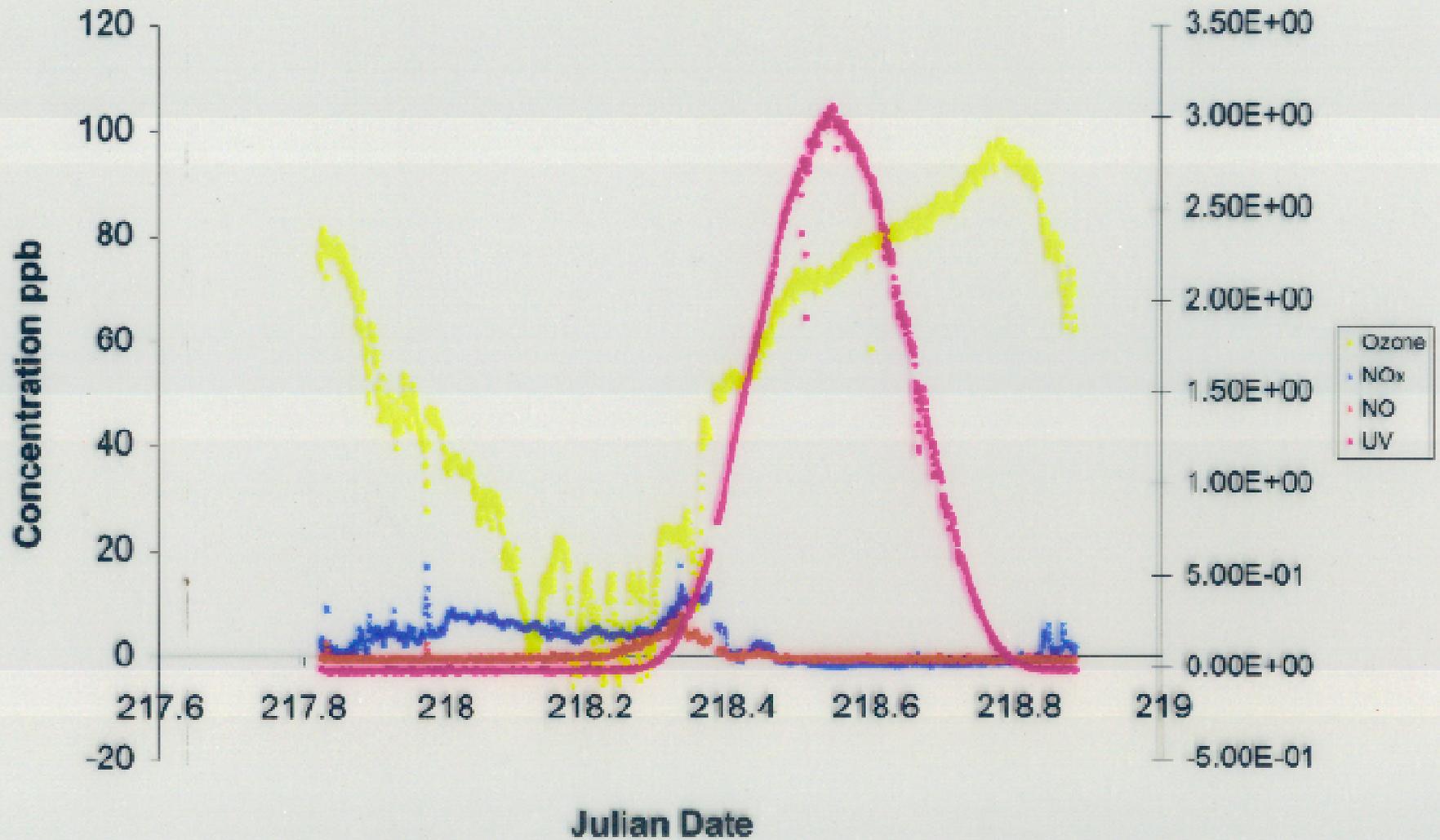


**CHEMILUMINESCENT SIGNAL:**

**~425 nm**

# NEOPS - Centerton, NJ

RAW DATA

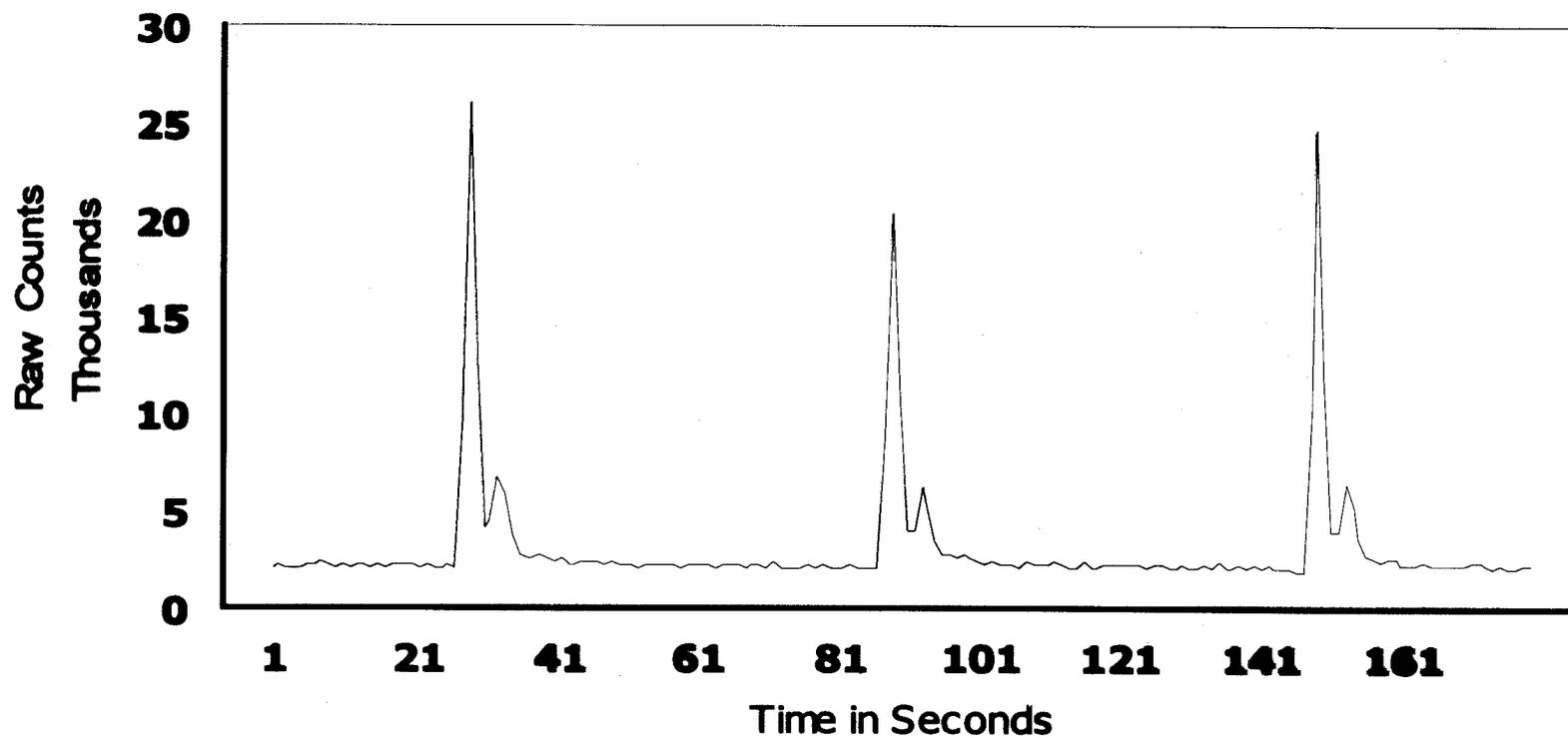


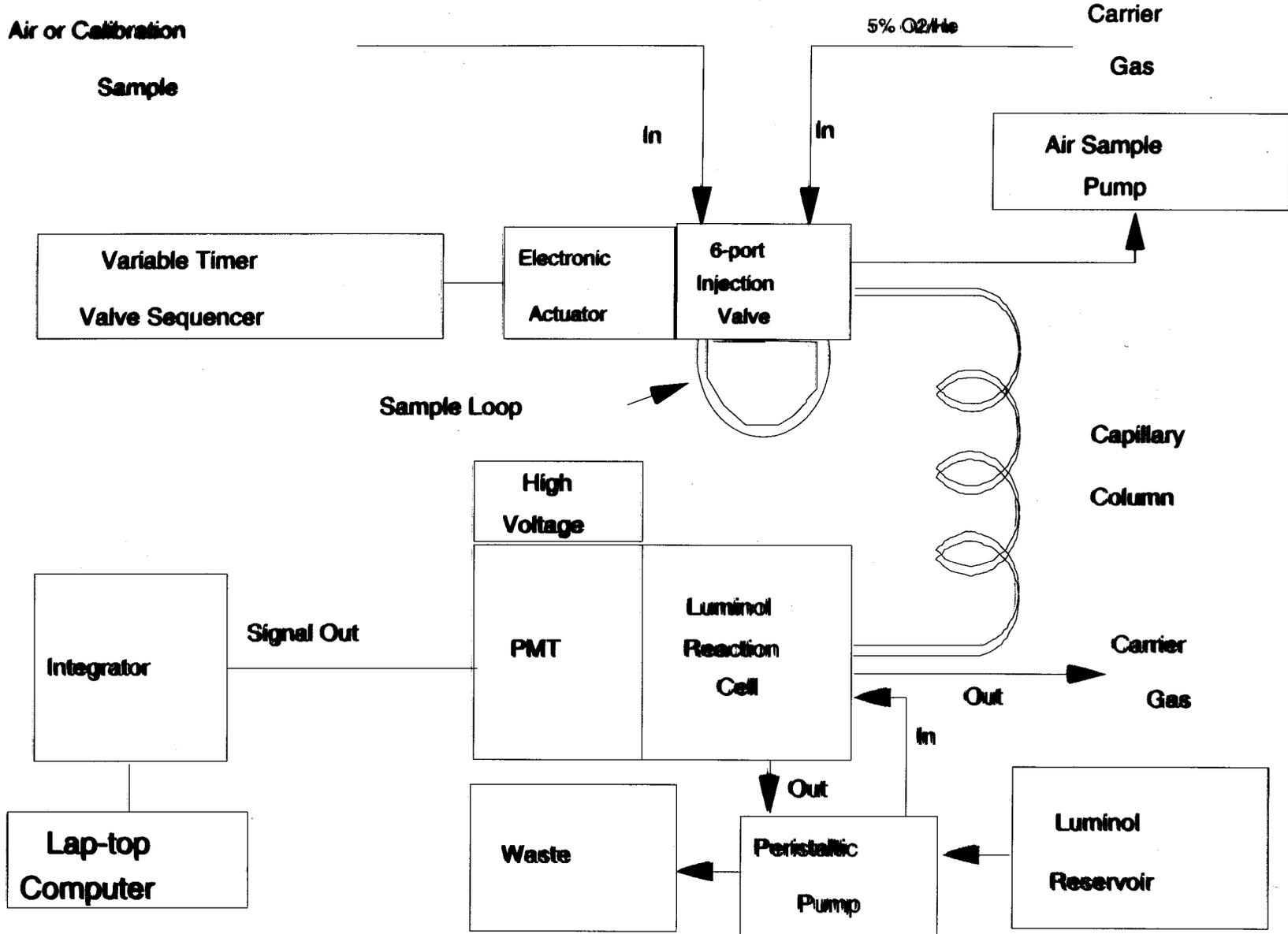
# NEOPS - Centerton, NJ

## Luminol Detection of NO<sub>2</sub>/PAN

30s time resolution

Figure 2. Raw Data from Vineland, NJ, 7/30/99, 11:39 to 11:41 am EDT.

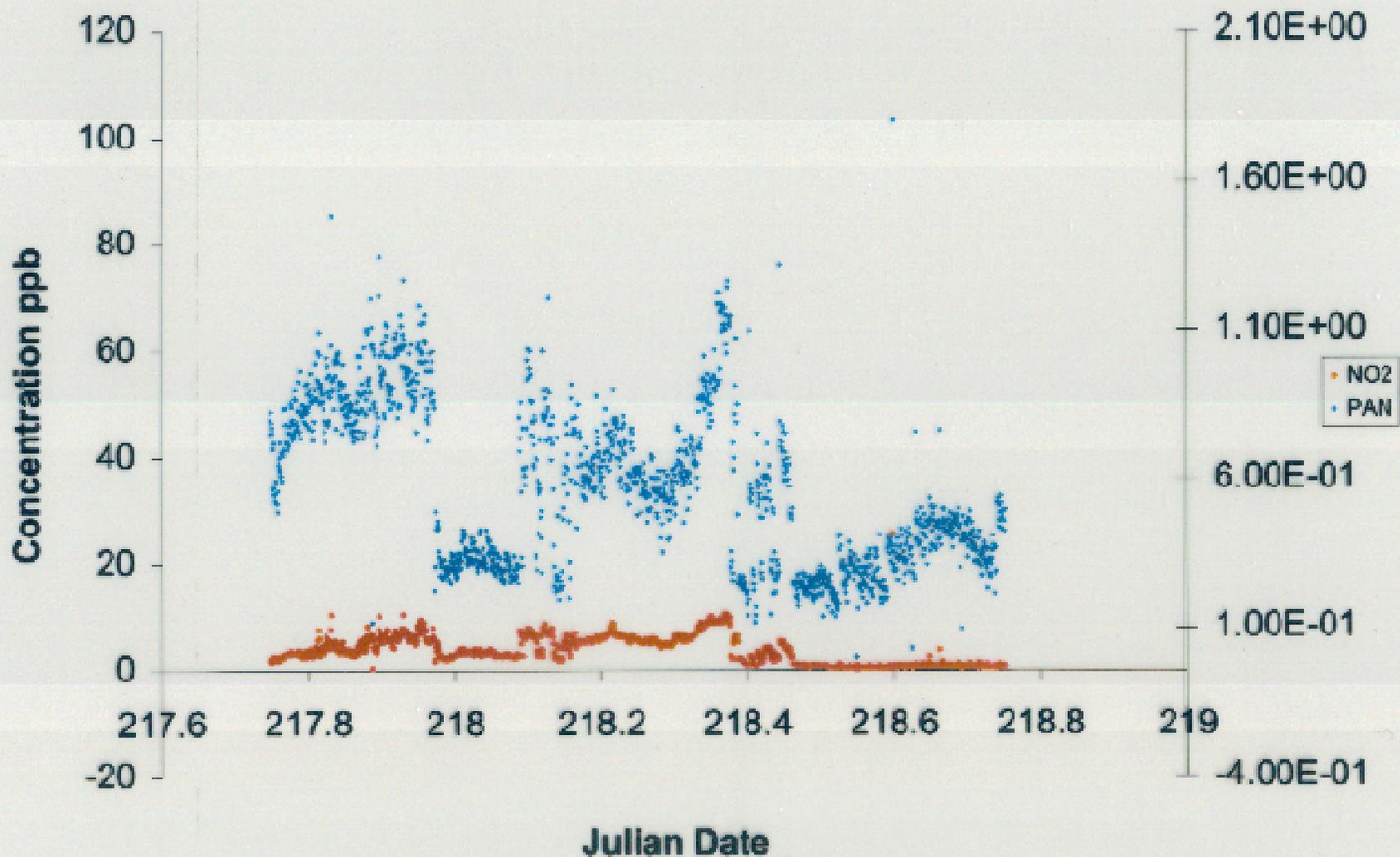




# NEOPS - Centerton, NJ

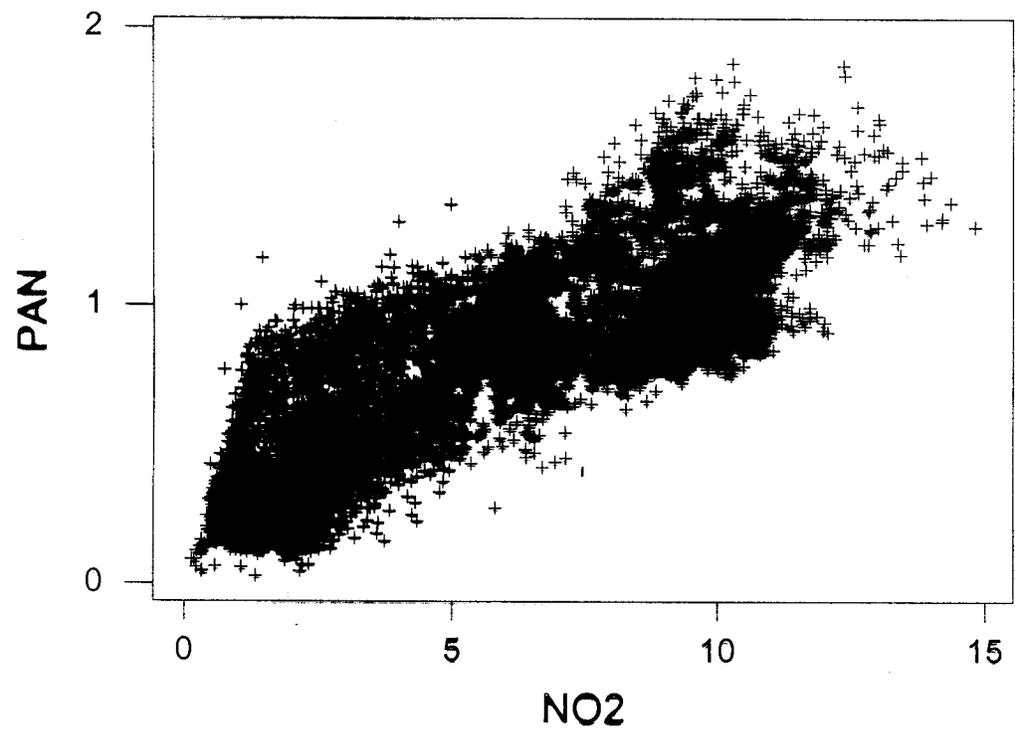
## Luminol Detection System

### NO<sub>2</sub> and PAN



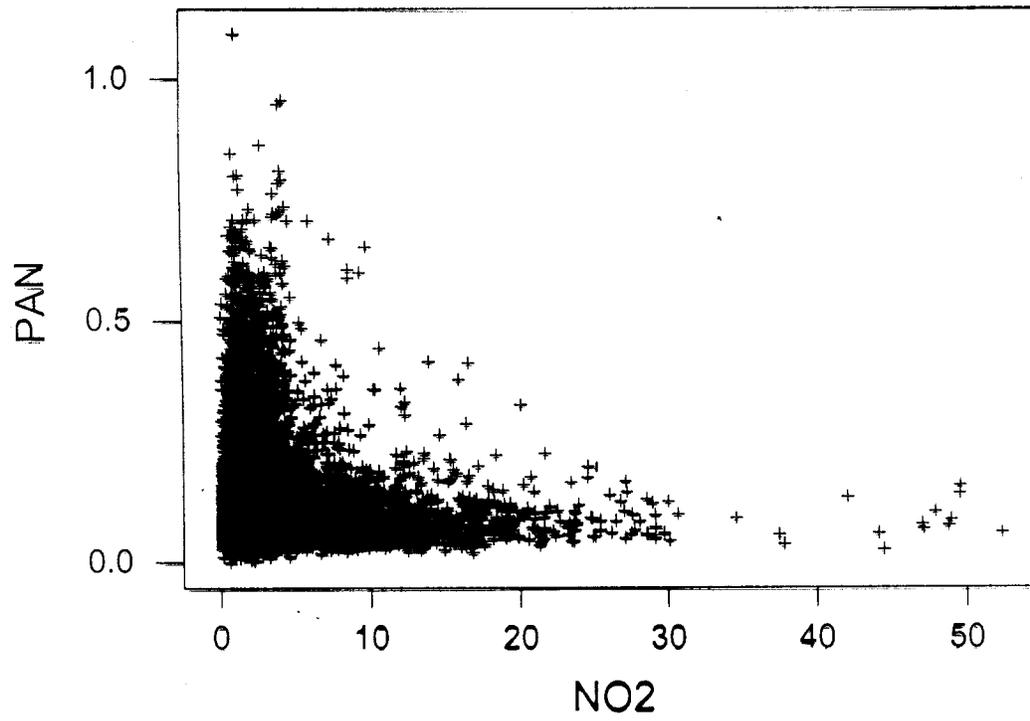
1N

### New Jersey

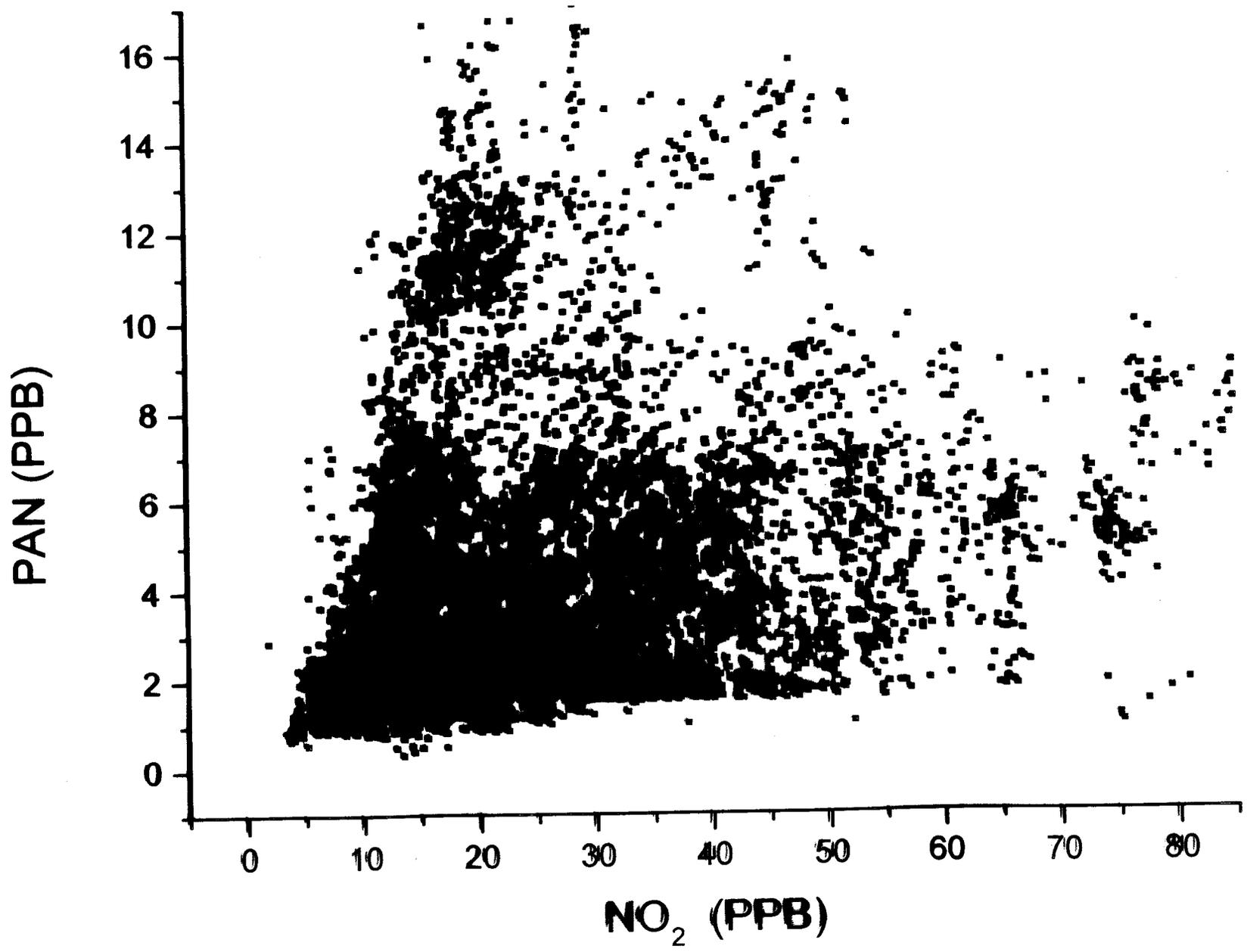


1P

### Phoenix



# DEER PARK (Texas 2000)



## **PAN and NO<sub>2</sub> with Fast GC/Luminol Detection**

*Atmospheric Environment*, **32**, 1145-1154 (1998).

*Environ. Sci. Technol.*, **33**, 3285-3289 (1999).

Proceedings Sixth US/German Workshop on Ozone/Fine Particle Science, Mission Inn, Riverside, California, October 4-6, 1999, EPA/600/R-00/076, October 2000, Basil Dimitrides, Ed., pp. 110-117 (2000).

Paper TS1-17. The 37th Western Regional Meeting , October 29-31, 2001. WERM: "An Earth Odyssey." Nobel Symposium Atmospheric Chemistry Abstract, pp. 99-100, 2001.

**LATEST VERSION OF INSTRUMENT  
– MARCH 2002**



2/13/1999 18:28



**Aerosol Radioactivity –  $^7\text{Be}$  and  $^{210}\text{Pb}$ ,  
 $^{210}\text{Bi}$ ,  $^{210}\text{Po}$ .**

*Aerosol Science and Technology*, **32**,  
569-583 (2000).

NETL – DATA for Pittsburgh –  $^7\text{Be}$  and  
 $^{210}\text{Pb}$  and  $^{210}\text{Po}$  – 24 hour –  $> 1 \mu\text{m}$

$^7\text{Be}$  – DATA for Deer Park – Phoenix  
2001

stratosphere

tropopause

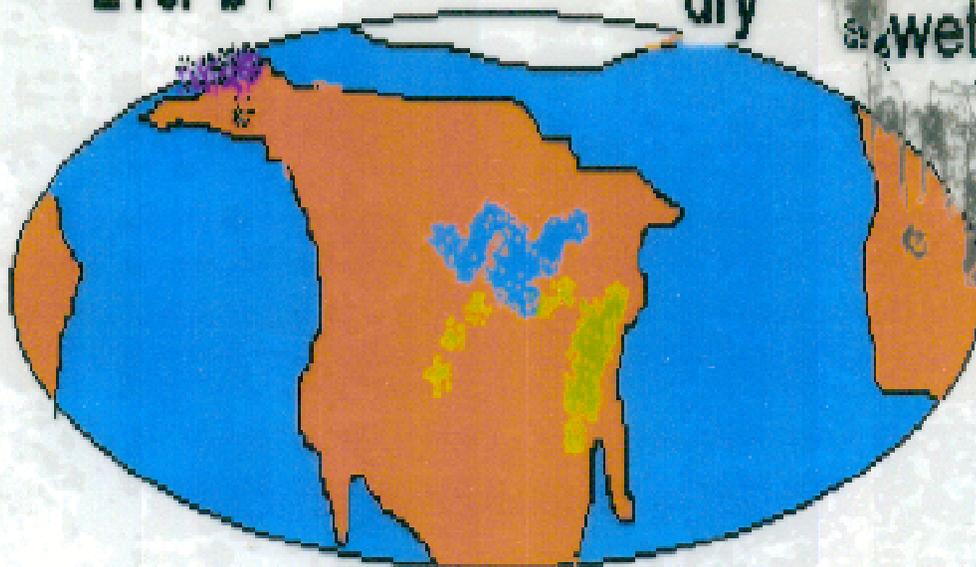
$7\text{Be}$

aerosols

$210\text{Pb}$

dry

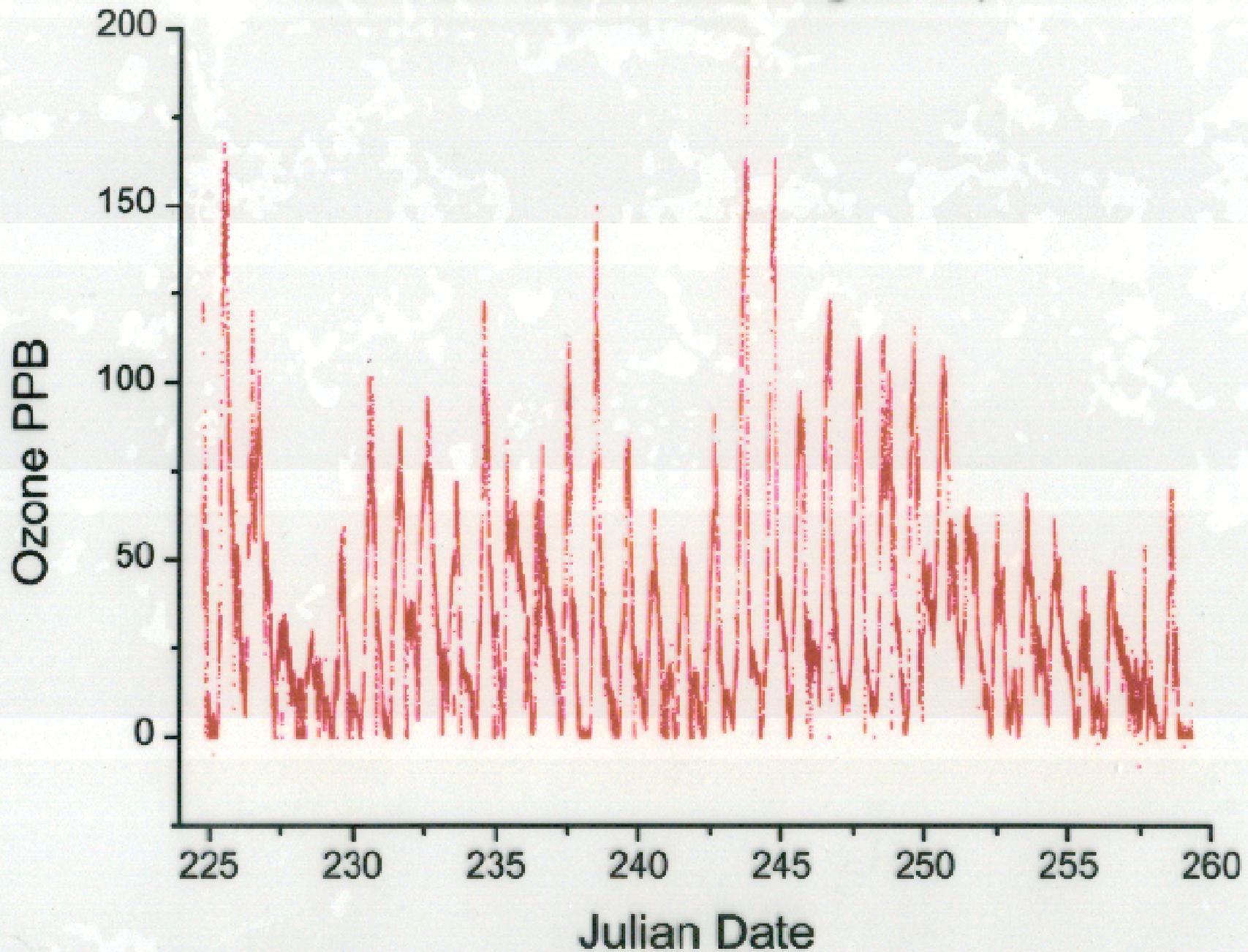
wet

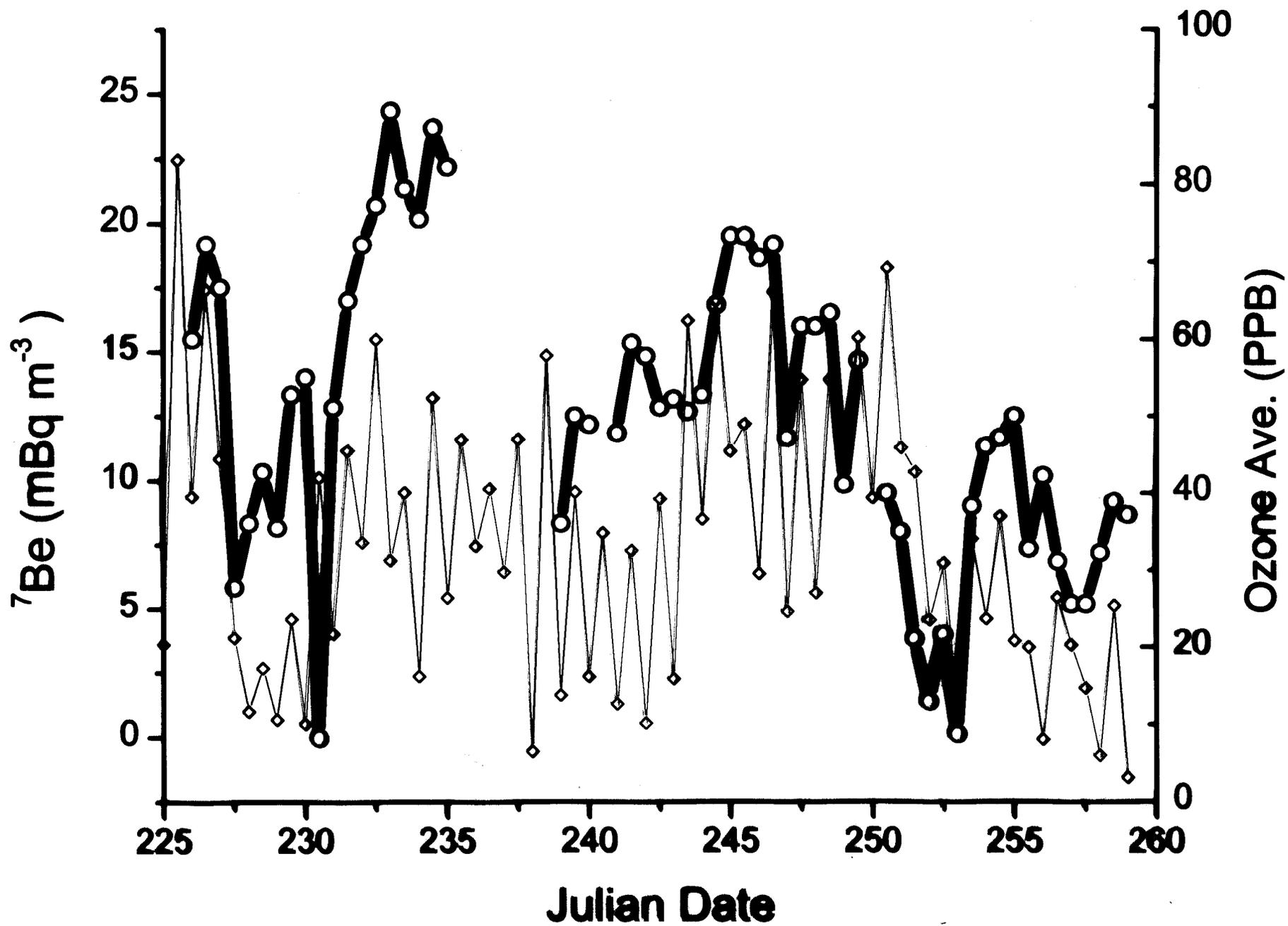


## Beryllium-7

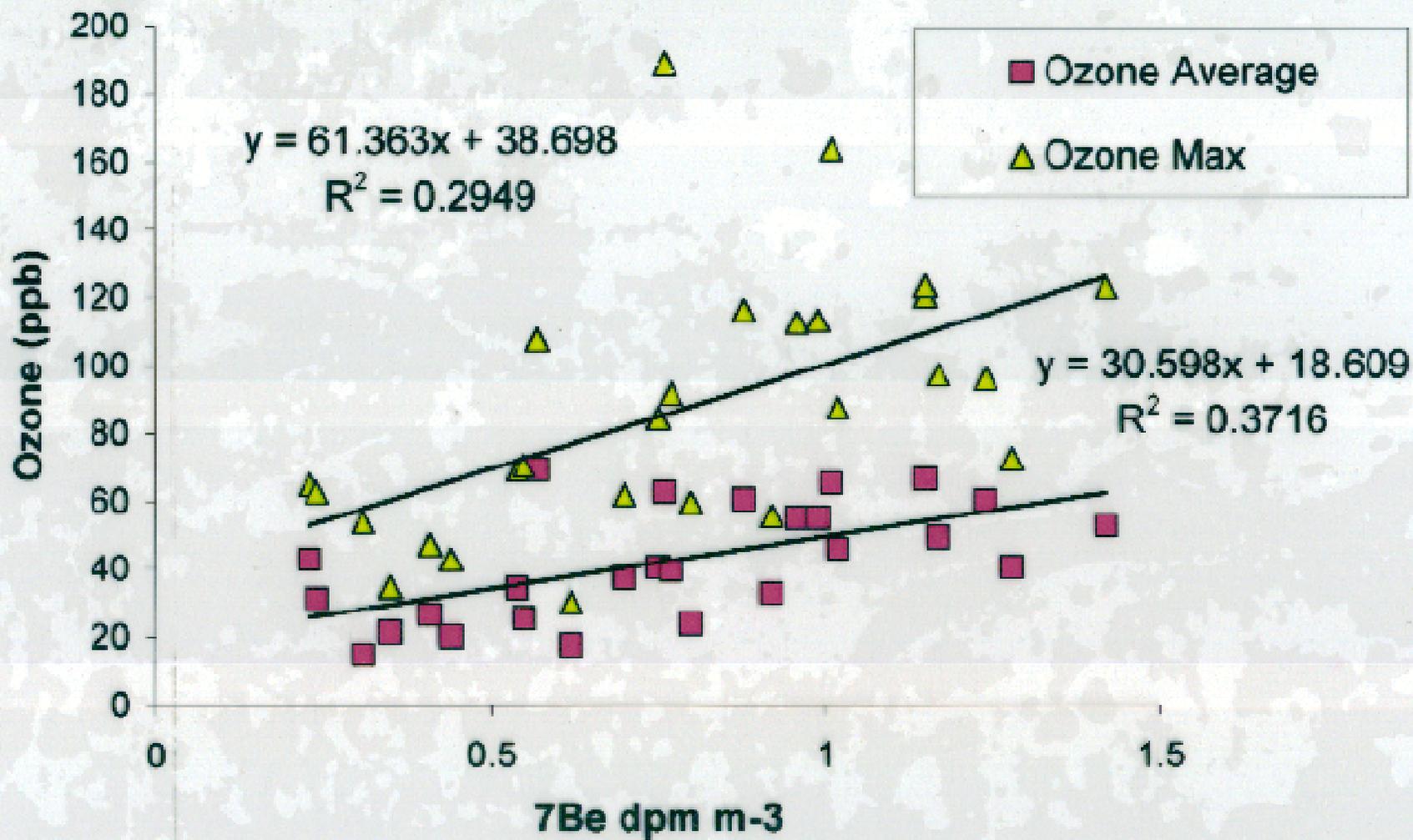
- Be-7 → 53.28 day half-life
- Natural radioactive isotope
- Cosmogenically produced in the atmosphere by spallation. (peak production at about 15km)
- Tropospheric production fairly independent of latitude (mean concentration > at 30°N and above).
- Once produced, these atoms rapidly attach to aerosols in the submicron range. (1.05μ and < )
- 10.4% of the actual disintegration emitted by gamma(γ) decay.
- Serves as a marker for upper tropospheric and lower stratospheric air that can be transported downward to surface levels. (i.e. a sensitive indicator of intrusions of stratospheric air into the troposphere)

# Deer Park - Ozone Data August-Sept. 2000

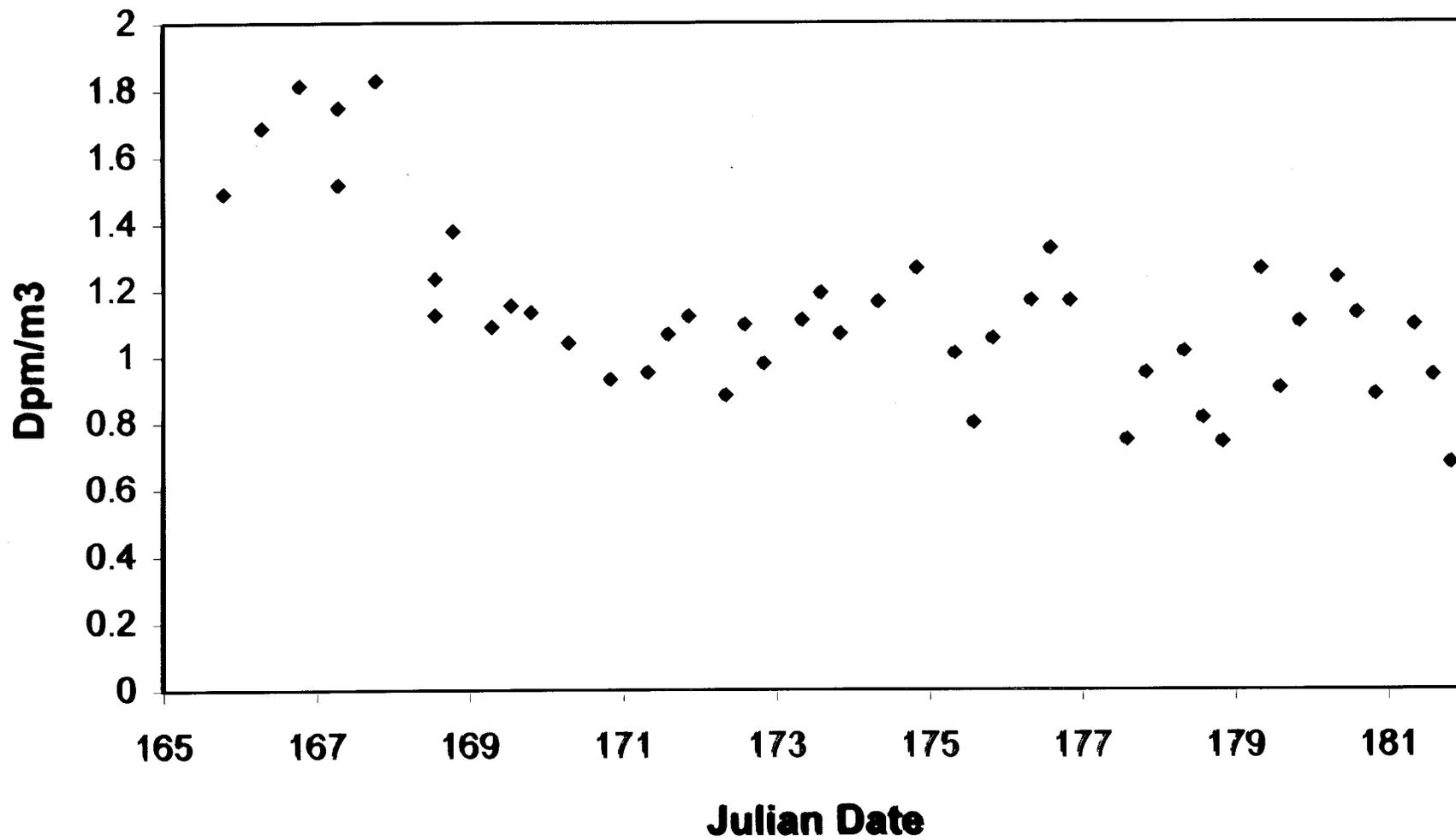




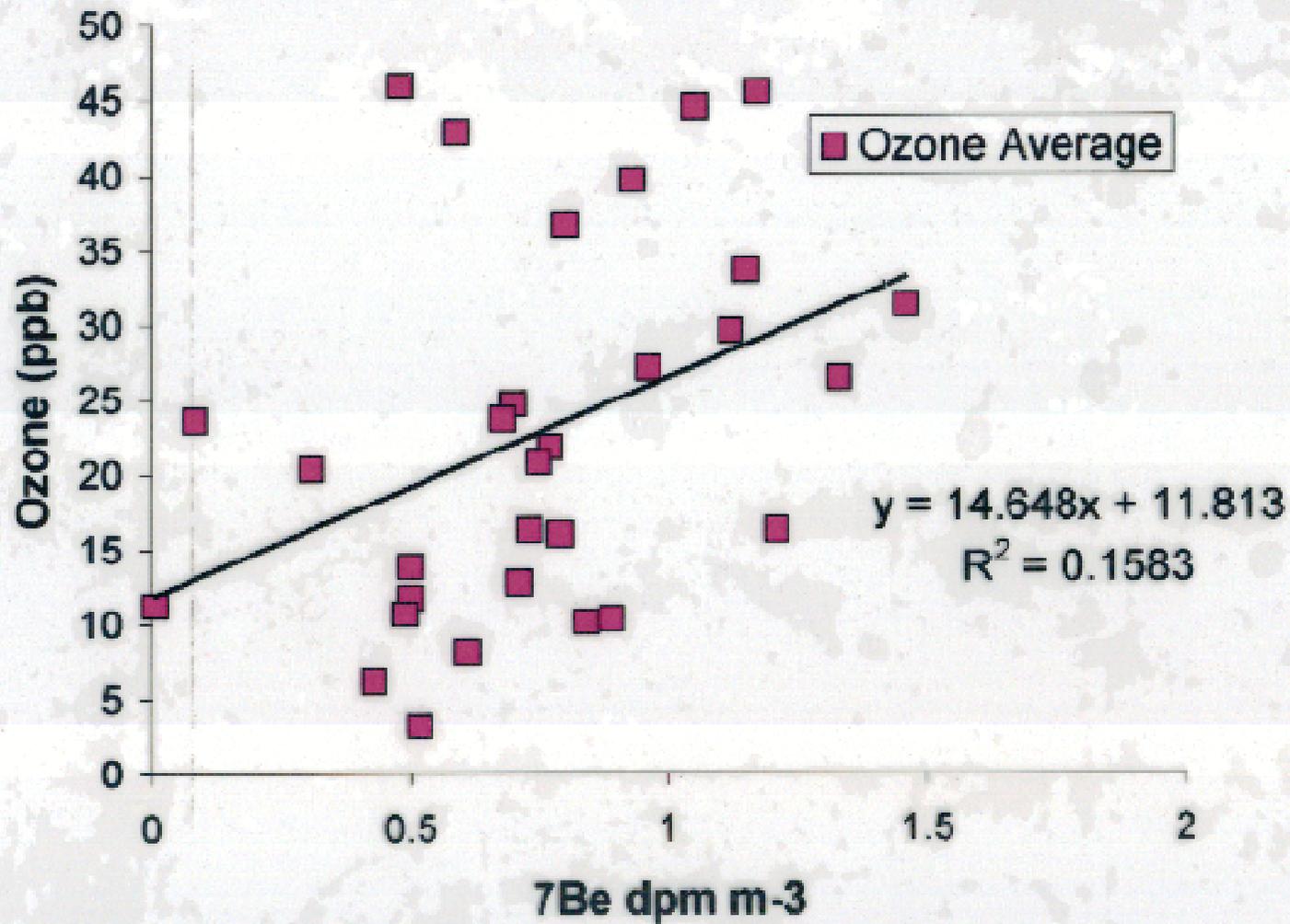
# 12 Hour 7Be - Daytime - Deer Park, TX



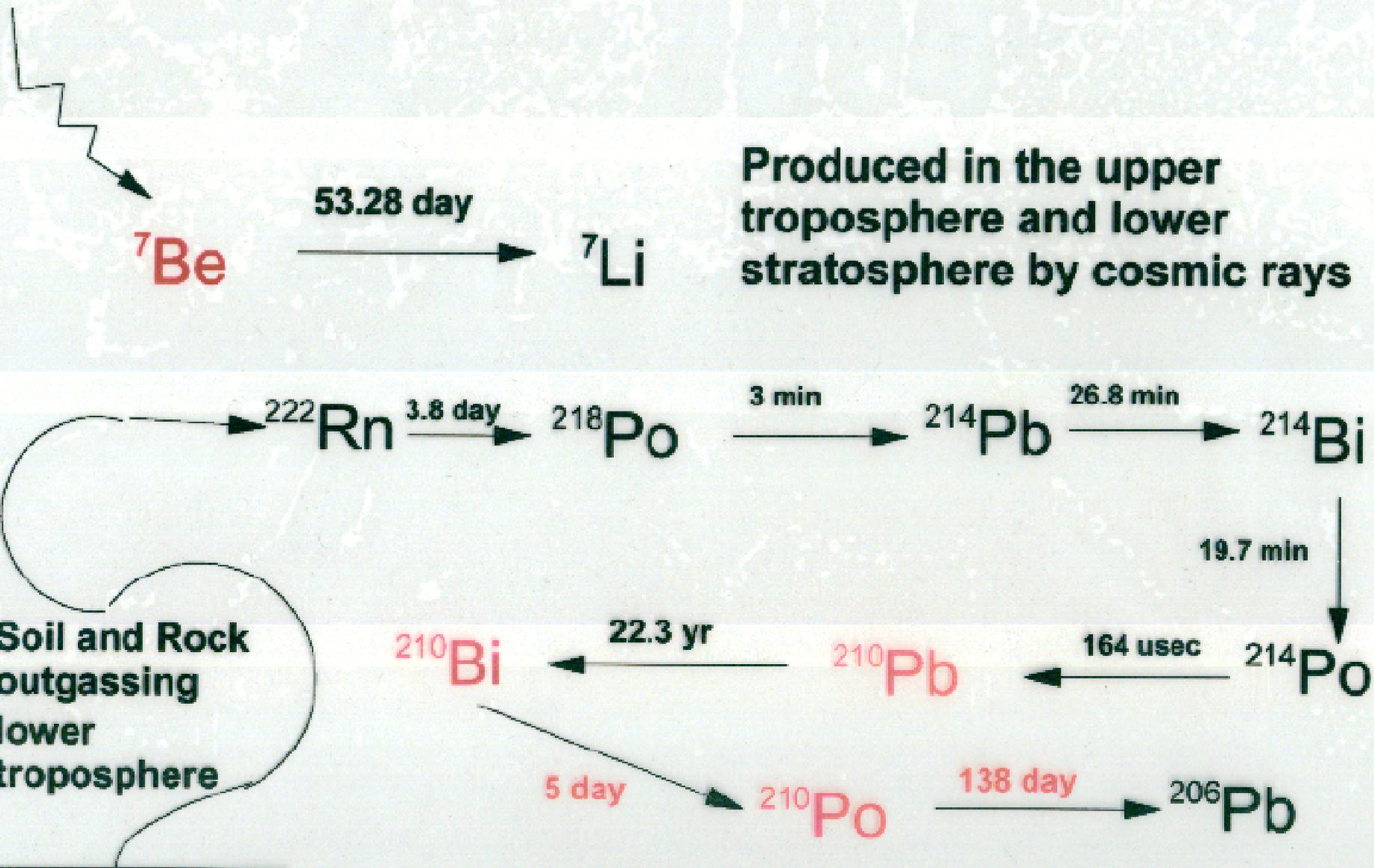
# PHOENIX 2001 Be-7 Dpm/m<sup>3</sup> vs Julian Date



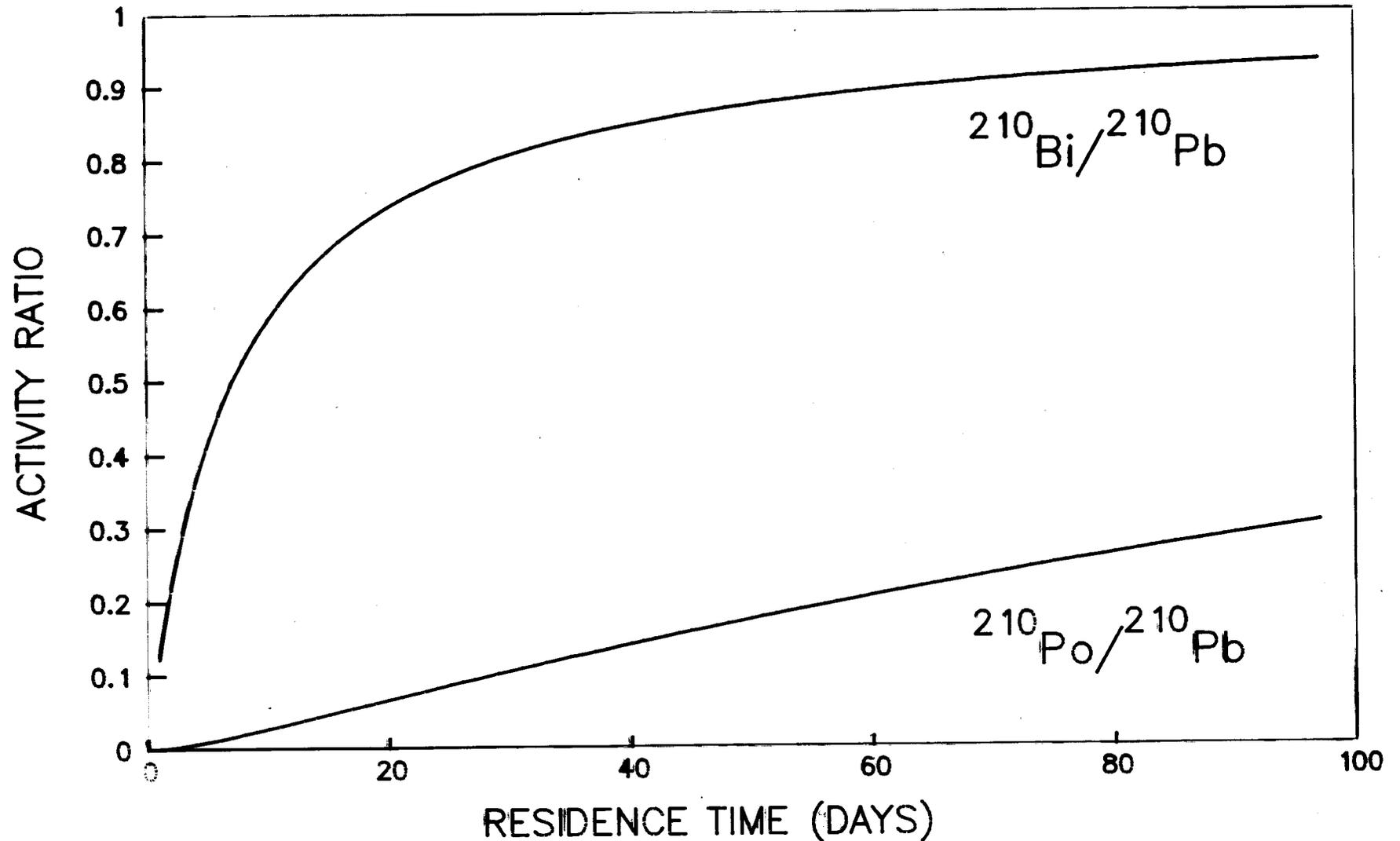
### 12 hour Nighttime 7-Be - Deer Park Texas



# Radioactive Decay of Natural Atmospheric Tracers



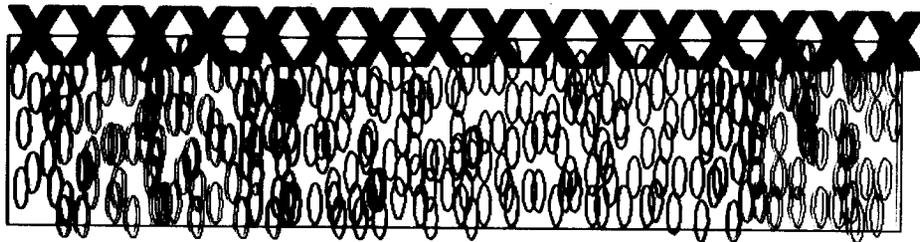
# Activity Ratio vs Residence Time for Aerosols Removed in Precipitation



(adopted from Nevissi, A.E. 1991, J. Radioanal. Nucl. Chem.)

# ADVANTAGES OF MEMBRANE FILTERS

Small anion exchange beads— high surface area  
Size — Amenable for Direct Counting  
Reasonably high flow rates



Mostly Surface Deposited

Beta Counting Efficiency — Bi-210 — 40%

Alpha Counting Efficiency — Po-210 — 17%

# Residence Times Calculated from $^{210}\text{Bi}/^{210}\text{Pb}$ Activity Ratios

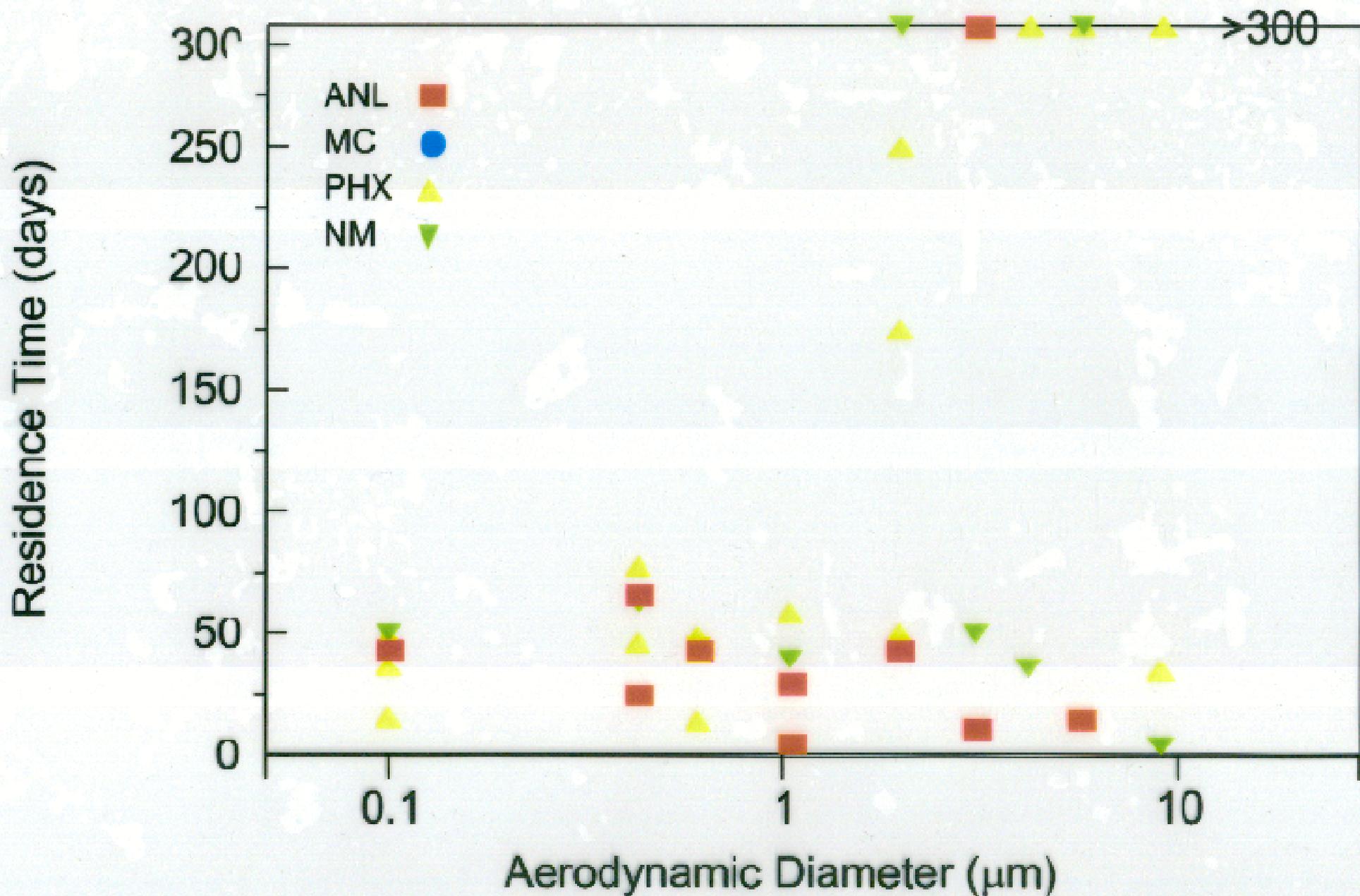
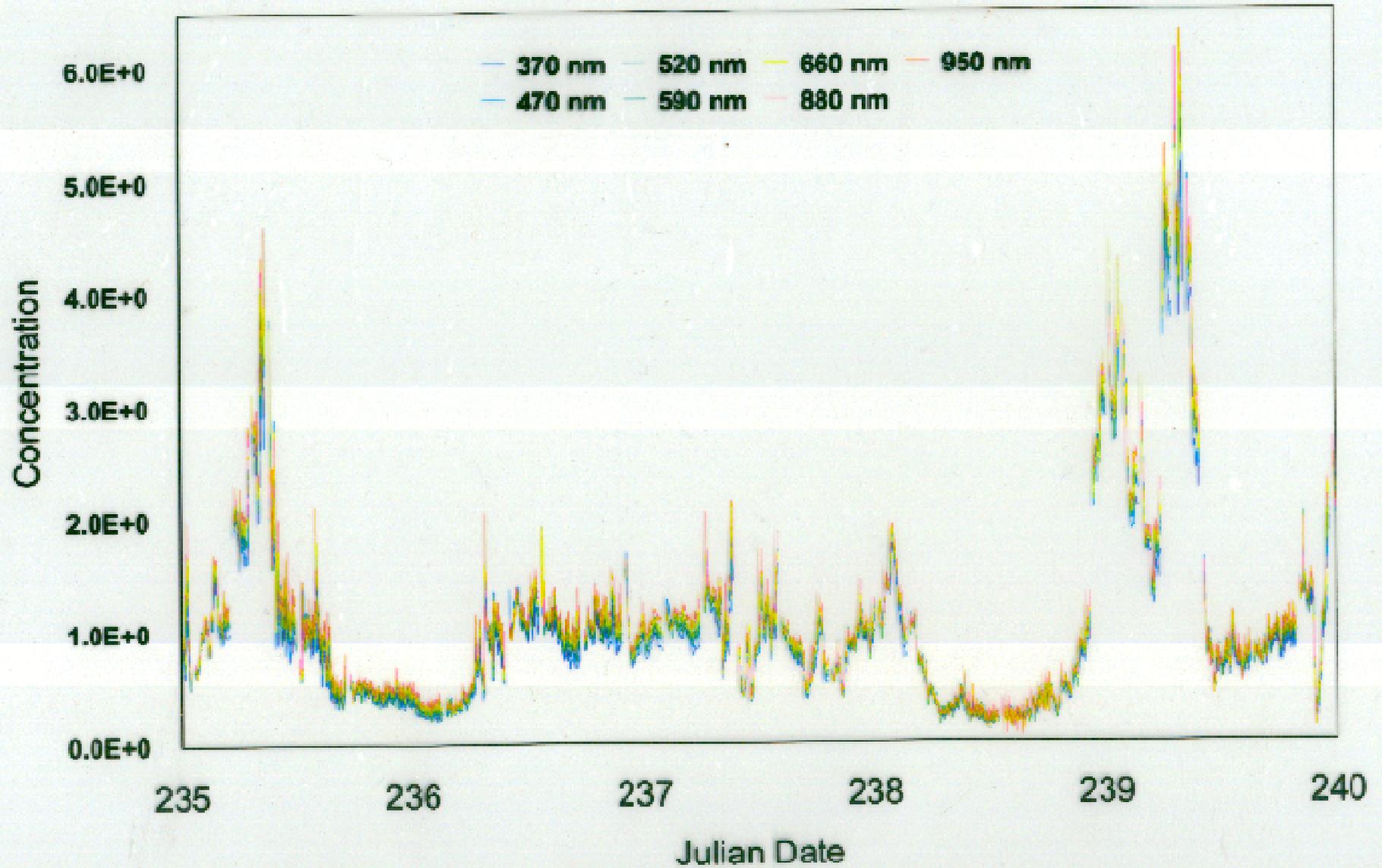


Table 1. Aerosol residence times calculated from the  $^{210}\text{Po}/^{210}\text{Pb}$  ratios for samples collected at Centerton.

Date in 1999	D ( $\mu\text{m}$ )	$^{210}\text{Po}/^{210}\text{Pb}$	Age (days)
7/24-7/30	9.2	0.112	32
	5.8	0.139	39
	4.2	0.142	40
	3.1	0.107	31
	2.0	0.177	50
	1.05	0.156	44
	0.62	0.125	35
	0.43	0.101	29
	0.1	0.132	37
	7/30-8/6	9.2	0.131
5.8		0.095	27
4.2		0.144	41
3.1		0.159	45
2.0		0.106	30
1.05		0.156	44
0.62		0.094	27
0.43		0.085	25
0.1		0.069	20
8/6-8/12		9.2	-
	5.8	0.156	44
	4.2	0.137	39
	3.1	0.125	35
	2.0	0.129	36
	1.05	0.133	37
	0.62	0.110	31
	0.43	0.136	39
	0.1	0.138	39

# Aethalometry

Chicago, IL (2001)



## **OBSERVATIONS**

**Excess  $^{210}\text{Po}$  is in the small size fractions.**

**$^7\text{Be}$  and  $^{210}\text{Pb}$  track each other. Both are associated with the fine aerosol fractions.**

**Recent modeling of  $^7\text{Be}$  and  $^{210}\text{Pb}$  deposition data using GCM's uses lower atmospheric lifetime of 9 days and upper atmosphere residence time of 23 days to best fit data. (Koch, Jacob, Graustein, JGR, 1996).**

**Are 5-6 day residence times reasonable for fine particles?**

## CONCLUSIONS

Aerosol residence times – 5-80 days - Long range transport will be important

Wind blown dusts are in the 2.5-10 micron range – Look Old –  
 $^{210}\text{Po}$  in equilibrium with  $^{210}\text{Bi}$  and  $^{210}\text{Pb}$

$^{210}\text{Po}/^{210}\text{Pb}$  and  $^{210}\text{Bi}/^{210}\text{Pb}$  can be used as tracers

$^7\text{Be}$  data tags upper troposphere – stratosphere sources

Mexican Fires – No indication of excess  $^{210}\text{Po}$

Coal Fly Ash – Should be enriched in  $^{210}\text{Po}$  and  $^{210}\text{Bi}$

- Source Characterization Needed to Resolve Source

## **Future Work:**

**TDLAS – Formaldehyde – Ammonia**

**Hinds Laboratory Roof Top Studies!**

**Particle/Gas (Oxidant) Interactions –  
Asthma?**

## **Acknowledgements**

**Nancy Marley – ANL**

**Mary Cunningham – Argo H.S. / ANL**

**Kent Orlandini – ANL**

**John Frederick – U of Chicago**

**Shelby Winiecki – U of Chicago**

**Victor Rodriguez – U of Puerto Rico**

**U.S. DOE – OBER- Mr. Peter Lunn**